EFFECT OF POLYVINYLPYRROLIDONE ADDITIVE ON THE PERFORMANCE OF HOLLOW FIBER ION EXCHANGER MIXED MATRIX MEMBRANE FOR COPPER REMOVAL

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ABSTRACT

The existence of copper in the environment is a concern due to the acute and long term toxicity. With the advantages of lower capital cost, easy operation process and high copper removal percentage, ion exchange technology offers the best treatment for copper removal but it has a drawback where it will cause a vast drop in pressure. In order to overcome this limitation, an ion exchanger mixed matrix membrane was produced in this study. Amberlite IR 120H cation exchanger was incorporated in the polyethersulfone (PES) based polymer solution. The effect of polyvinylpyrrolidone (PVP) pore forming additive in the PES dope solution was studied in the range of 0 to 10wt%. The hollow fiber membrane was synthesized using dry-wet spinning procedure. The pore structure of the membrane was characterized using Scanning Electron Microscope (SEM) and was found more porous as the concentration of PVP increases. The permeability was also increased as the concentration of PVP increases. The optimum concentration of PVP for the removal of copper is between 3wt% and 5wt%.

ABSTRAK

Kewujudan kuprum dalam alam sekitar adalah kebimbangan disebabkan oleh ketoksikan jangka akut dan panjang. Dengan kelebihan kos modal yang lebih rendah, proses operasi yang mudah dan tembaga tinggi peratusan penyingkiran, teknologi pertukaran ion menawarkan rawatan yang terbaik untuk penyingkiran kuprum tetapi ia mempunyai kelemahan di mana ia akan menyebabkan penurunan besar dalam tekanan. Dalam usaha untuk mengatasi had ini, ion membran penukar matriks bercampur dihasilkan dalam kajian ini. Amberlite IR 120H kation penukar diperbadankan pada polyethersulfone yang (PES) penyelesaian polimer berasaskan. Kesan polyvinylpyrrolidone (PVP) liang membentuk bahan tambahan dalam larutan PES telah dikaji dalam julat 0 hingga 10wt%. Membran gentian geronggang telah disintesis menggunakan prosedur berputar kering-basah. Struktur liang membran dicirikan menggunakan Mikroskop Imbasan Elektron (SEM) dan didapati lebih poros sebagai kepekatan kenaikan PVP. Kebolehtelapan ini juga meningkat kepekatan kenaikan PVP. Kepekatan optimum PVP untuk penyingkiran tembaga adalah antara 3wt% dan 5wt%.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

Greek

ν_l	kinematic viscosity

Subscripts

g	gas
l	liquid
eff	effective

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
$CuSO_4.5H_2O$	Copper Sulphate Pentahydrate
NMP	N-Methyl-2-pyrrolidone
PAM	Polyacrylmide
PAN	Polyacrylite
PEG	Polyethylene glycol
PES	Polyethersulfone
PVDF	Polyvinyllidene fluoride
PVP	Polyvinylpyrrolidone
SEM	Spectrometry Electron Microscope

1 INTRODUCTION

1.1 Motivation and statement of problem

Abundant of heavy metals waste water has been generated worldwide due to the industry activities such as mining, metals plating, electric device manufacturing, surface treatment and raw material for synthesis. Heavy metals such as copper, lead, mercury and chromium are toxic to human as it compromises acute and long term effect to our health(Farooq, et al., 2010).

Copper is vastly used as the major material of electronic industries. It is one of the most common metals be used in industries for the construction of structures as it has a relative high tensile strength (Kuhn & Medlin, 2000)

As a result of application of copper in electronic industries, it generates an environmental problem as the heavy metals are toxic, environment persistent and have the tendency to accumulate in the body tissues (Al-Rashidi, et al., 2013).

Membrane technology in the separation processes have became one of the emerging technologies which experienced a rapid growth of during the past decades. The membrane technology has been widely used in the gas separation where heat is not required or the mixture is an azeotrope (Hillmen, 2000). In the removal of heavy metals, membrane is not widely used as the dead end filtration is prone to fouling and concentration polarization (Zhang & Vecitis, 2014).

Several processes have been practiced for the removal of heavy metals. These methods include chemical precipitation, ion-exchange, membrane filtration, carbon adsorption, co-precipitation/adsorption and electrochemical removal (Babel & Kurniawan, 2003). Ion exchange processes mostly uses selective chelating resins contain anion functional group that have affinity towards the heavy metals ions. Besides that, the ion exchange resins causes a vast drop in pressure as the treated water passes through the ion exchange bed filled with resins (Stremovskii & Klyueva, 1974).

To date, the removal of heavy metals from wastewater using membrane are mostly flat sheet profile (Sato, et al., 2002). Microfiltration and nanofiltration are unique due to the

separation mechanism which is working based on size exclusion, charge repulsion and have a higher rejection of multivalent heavy metals ions as compared to UF membranes. (Gherasim, et al., 2013). Recently hollow fiber has become a progress due to the high total surface area as compare to flat sheet (Peng, et al., 2012).

1.2 Objective

The objective of this research is to study the effects of polyvinylpyrrolidone additive concentration on the performance of hollow fiber ion exchanger mixed matrix membrane for copper removal.

1.3 Scope of this research

The following are the scope of this research:

i) To produce ion exchange hollow fiber MMM by incorporating cation resin, Amberlite IR120H into a polymer solution consist of PES, NMP and PVP.

ii) To study the effect of PVP additive concentration in the PES-Amberlite IR120H dope polymer solution from 0-10wt% on the performance of adsorptive MMM for copper removal.

iii) To characterize the MMM in term of pore structure, water permeability and static adsorption properties for copper removal.

iv) To study the effect of pH on the adsorption capacity of the membrane.

1.4 Main contribution of this work

The following are the contributions:

1) To provide an economic alternative for the removal of copper from the wastewater.
2) To provide a more efficient alternative for the removal of copper.
3) To enhance the quality of water in order to reduce the pollution of the river caused by the electronic industries in Malaysia.

1.5 Organisation of this thesis

This thesis was distributed into five chapters. Following the introduction in Chapter 1,

Chapter 2 provides a description of the applications and general design features of ion exchanger mixed matrix membrane (MMM). A general description on the hollow fiber membrane, as well as the ion exchange and adsorptive membrane. This chapter also provides a brief discussion of the advanced experimental techniques available for copper removal, mentioning their applications and limitations for permeability and adsorption analysis. A summary of the previous experimental work on copper removal is also presented. A brief discussion on the characterisation methods for Ion Exchanger Mixed Matrix Membrane is also provided.

Chapter 3 is essential as it provides the information on the materials and methods of synthesizing and characterising the Ion Exchanger Mixed Matrix Membrane for Copper Removal. The performance of the Ion Exchanger Mixed Matrix Membrane (MMM) for Copper Removal with different concentration of Polyvinlypyrrolidone (PVP) additive range from 0-10wt% will be explained. The performance of the Ion Exchanger MMM was studied based on the permeability, adsorption and structure. The experimental data were compared to determine the optimum concentration of the PVP. Both static and dynamic adsorptions of the copper by the ion exchanger were studied.

Chapter 4 focused on the major findings of this research with relevant discussion. The first section will be discussing about the characterized membrane developed in this research using SEM and permeability. The effect of pH on the membrane was also discussed. The performance of the membrane is discussed based on the static and dynamic adsorption capacity and elution recovery. The analysis was done based on the data obtained.

Chapter 5 is focused on the conclusion and recommendation of the dissertation based on the results and discussion.

2 LITERATURE REVIEW

2.1 Heavy Metals Pollution

Heavy metals in industrial wastewater effluent are mainly from the heavy industries. Heavy metals are toxic and non-biodegradable and may have the continuity to exist in our water bodies. The release of heavy metal to the environment has effect on both aquatic and land organisms as heavy metals inhibits the activity of most biological body that resulting maybe acute or chronic effect to the health. Furthermore, heavy metals are not easily removed from the body. Hence a strict environmental regulation has been legislated to mitigate the heavy metals contamination especially in the discharge of industrial effluent that contains high concentration of heavy metals. The Table 2.1 shows the limits of Standards A and B that includes the limits for heavy metals. The heavy metal that is chosen to be studied is copper as it is common in our wastewater. The following Figure 2.1 and Figure 2.2 show the concentration of copper in the various sampling stations in Malaysia in year 2009. It is found out that only two of the station readings comply with the acceptable limits of Standard A for copper which are 0.20mg/L and 1.0mg/L. Whereas in compliance of Standard B, there are a few that did not comply with the reading as high 20.60mg/L which is four times the limit of 5.00mg/L of Standard B for Iron acceptance level.

Table 2.1: Parameter Limits of Effluent of Standards A and B **(Department of Enviroment, 2000)**

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT OR MIXED EFFLUENT OF STANDARDS A AND B

	Parameter	**Unit**	**Standard**	
			A	**B**
	(1)	(2)	(3)	(4)
(i)	Temperature	^{o}C	40	40
(ii)	pH Value	-	6.0-9.0	5.5-9.0
(iii)	BOD at 20^{o}C	mg/L	20	50
(iv)	Suspended Solids	mg/L	50	100
(v)	Mercury	mg/L	0.005	0.05
(vi)	Cadmium	mg/L	0.01	0.02
(vii)	Chromium, Hexavalent	mg/L	0.05	0.05
(viii)	Chromium, Trivalent	mg/L	0.20	1.0
(ix)	Arsenic	mg/L	0.05	0.10
(x)	Cyanide	mg/L	0.05	0.10
(xi)	Lead	mg/L	0.10	0.5
(xii)	Copper	mg/L	0.20	1.0
(xiii)	Manganese	mg/L	0.20	1.0
(xiv)	Nickel	mg/L	0.20	1.0
(xv)	Tin	mg/L	0.20	1.0
(xvi)	Zinc	mg/L	2.0	2.0
(xvii)	Boron	mg/L	1.0	4.0
(xviii)	Iron (Fe)	mg/L	1.0	5.0
(xix)	Silver	mg/L	0.1	1.0
(xx)	Aluminium	mg/L	10	15
(xxi)	Selenium	mg/L	0.02	0.5
(xxii)	Barium	mg/L	1.0	2.0
(xxiii)	Fluoride	mg/L	2.0	5.0
(xxiv)	Formaldehyde	mg/L	1.0	2.0
(xxv)	Phenol	mg/L	0.001	1.0
(xxvi)	Free Chlorine	mg/L	1.0	2.0
(xxvii)	Sulphide	mg/L	0.50	0.50
(xxviii)	Oil and Grease	mg/L	1.0	10
(xxix)	Ammoniacal Nitrogen	mg/L	10	20
(xxx)	Colour	ADMI*	100	200

*ADMI-American Dye Manufacturers Institute

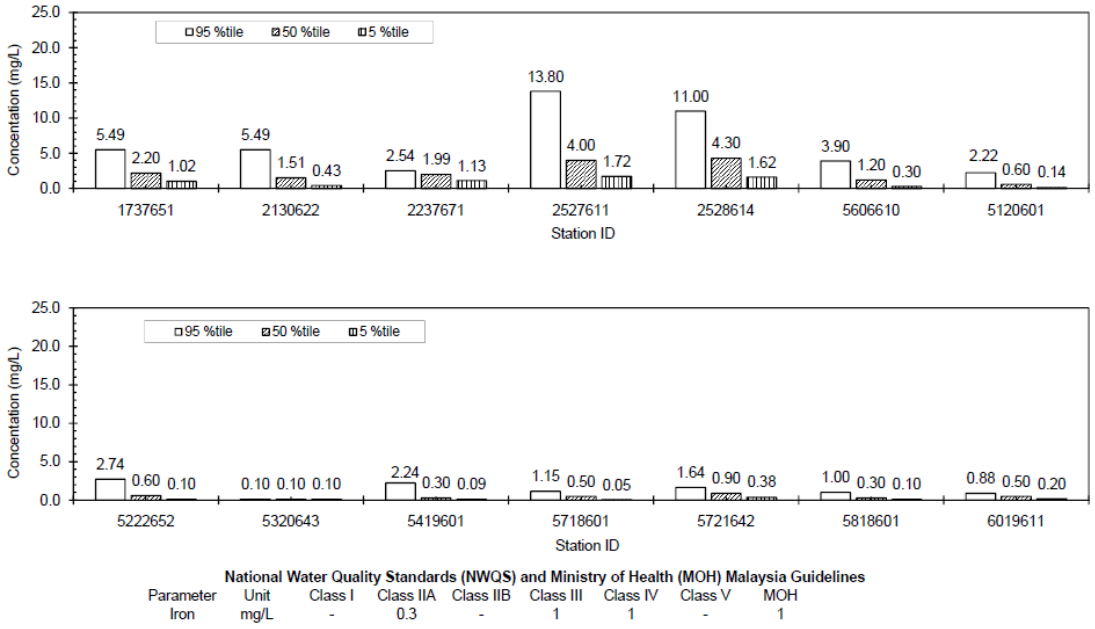

Figure 2.1: Percentile Values of Cu (Copper) at all Sampling Stations **(Department of Irrigation and Drainage, 2009)**

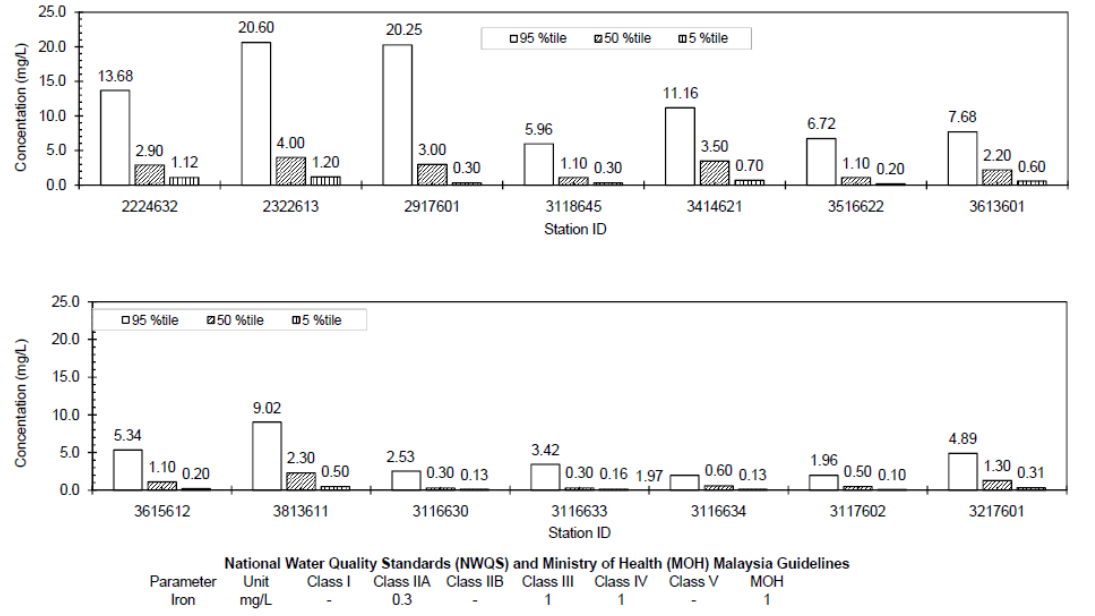

Figure 2.2: Percentile Values of Cu (Copper) at all Sampling Stations continued **(Department of Irrigation and Drainage, 2009)**

2.1.1 Copper

Copper is a ductile metal with a very high electrical and thermal conductivity. It is used as a conductor of electricity and heat, parts of several metal alloys and construction

material. It has been used for thousands of years. Copper compromises 50 parts per million in of the earth crust. Copper element can be found in the earth crust naturally and the Cu^{2+} ions are easily combine with sulphur and oxygen containing compounds such as hydroxides, oxides, carbonates and sulphides. Chalcopyrite and Chalcocite are the most common compound of copper found in nature. Copper (as Cu^{2+}) concentrations of 40 µg/litre can be detected by taste in distilled water. In mineralized spring water with total dissolved solids (TSS) content of 500 mg/litre, the taste threshold value was 0.12 mg/litre.

Copper is vital in human nutrition. The estimated of the minimum daily requirement for copper range from about 0.9 to 1.3 mg/day(FAO, 1988). The average lethal dose of copper is 10 mg/kg of body weight. Studies have shown that in excess of copper dosage can cause to tissue injury and disease. The oxidation potential of copper is responsible for some of its toxicity in excess ingestion cases that causes oxidative damage to the human body system that includes peroxidation of lipids and other macromolecules (Bremner, 1998). There's research that shows the significance of the excess of copper in the progression of Alzheimer's disease due to the accumulation of metal homeostasis disturbance that develops in individuals with Alzheimer's disease brains that possibly be damaging by the toxic buildup of amyloid beta in the brain (Bhattacharya, 2003).

2.2 Heavy Metals Removal Techniques

2.2.1 Adsorption

It is recognized as an economic and effective method of removing heavy method as it provides the flexibility of design and operation for the removal of heavy metals. In most cases, it is able to produce high quality treated heavy metals effluent. In addition, it is able to be regenerated through desorption process of the adsorbents. Activated carbon is the most widely used adsorbent to remove heavy metals. It is derived from carbonaceous source of material such as coconut husk, wood, coal and recently from biomass. It is produced through either chemical activation or physical activation. Activated carbon is extensively used in removal of heavy metals as it is highly porous and high surface are per volume. Langmuir and Freundlich are the two isotherms used to describe the application of water treatment. The Langmuir isotherm is

$$q = \frac{q_o c}{K + c}$$

(2.1)

In Langmuir isotherm, only a fixed number of active sites available for adsorption. It is also a reversible and reaches equilibrium.

The Freundlich isotherm is

$$q = Kc^n$$

(2.2)

In Freundlich isotherm, it explained the variation of adsorption with temperature. This isotherm is fails at higher pressure. The mechanism of adsorption is visualized in the Figure 2.3.

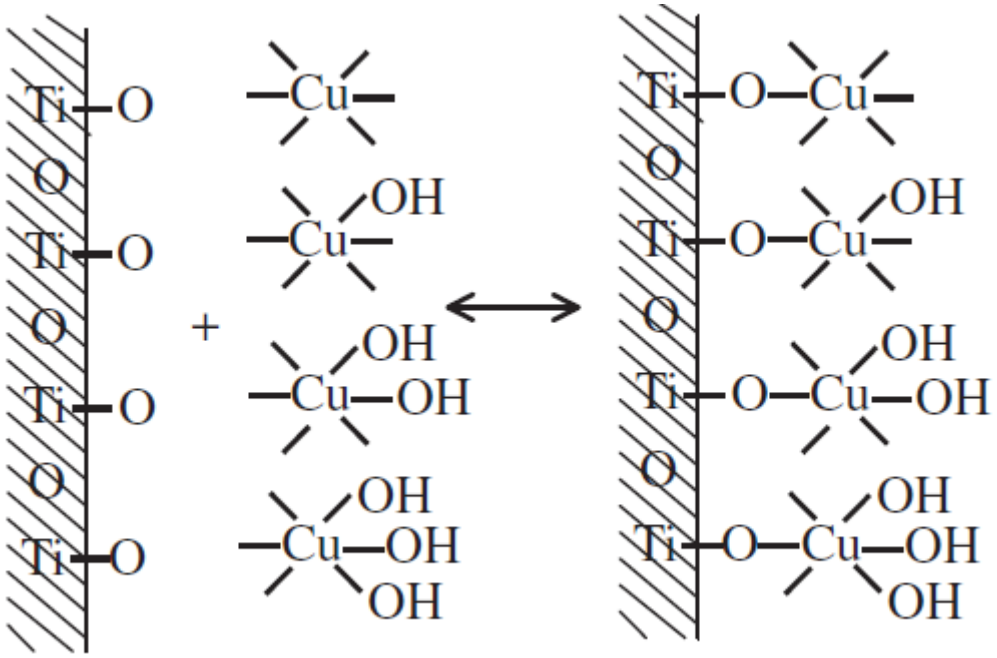

Figure 2.3: The adsorption mechanism of Cu(II) on hydrous TiO_2 **(Barakat, 2005)**

2.2.2 Chemical Precipitation

Chemical Precipitation the most widely used technique as it is inexpensive and relatively simple to operate (Ku & Jung, 2001). The chemicals react with heavy metals to form insoluble precipitates that will be then removed using filtration method. The chemicals widely used for precipitation are such as hydroxides and sulfides. Hydroxides are widely used as the pH control is easy (Huisman, et al., 2006). The range of the hydroxides is pH from 8.0-11.0. The metals hydroxides such as potassium hydroxides and sodium hydroxides can be removed using sedimentation and flocculation. In

addition, aluminum oxide and iron salts are being used to boost the removal of the heavy metals. The drawback of hydroxide precipitation is that it produces a large amount of sludge that poses disposal problems (Kongsricharoern & Polprasert, 1995).

Aside from metals hydroxides, sulfide precipitation is also an effective method to remove heavy metals. It is more preferred to be used due to the solubility of most sulfide compounds are less soluble as compare to hydroxides that provides a more effective removal of heavy metals. However, sulfide precipitation process is causing problems due to the hydrogen sulfide toxic fumes with the reaction of acidic conditions. Thus the process should be done in neutral or alkaline condition. Lastly, the sulfide precipitation is prone to form colloidal precipitates that causes problem in filtration and settling process.

Recently, chelating precipitants are used to precipitate heavy metals from the solution. The three widely used chelating precipitants for heavy metals removal are trimercaptotriazin, sodium dimethyl dithiocarbonate and potassium/sodium dimethyldithiocarbonate. Chelating precipitation is a particular method that ions and molecules bind metals ions to form precipitants and removed through filtration(Wang, et al., 2012). Chelating precipitation shows a remarkable result of reducing the concentration of heavy metals with an immediate reduction of the heavy metals but if the precipitate is not removed immediately, it will decompose and form by products such as tetramethylthiuram and thiram which are toxic to aquatic organisms (Atwood & Zaman, 2006). In Figure 2.4, shows the process of a conventional metals precipitation treatment plant.

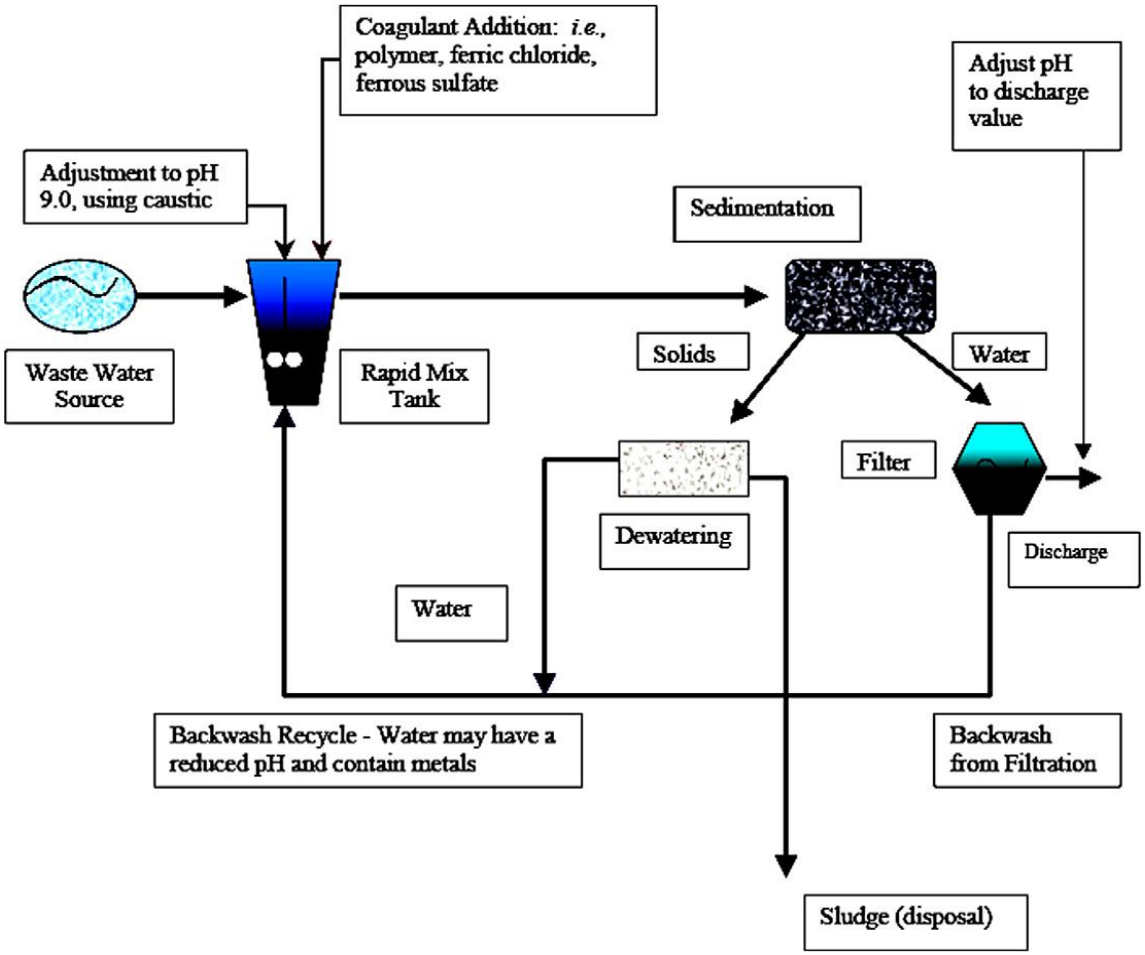

Figure 2.4: Processes of a conventional metals precipitation treatment plant **(Wang, et al., 2005)**.

2.2.3 Coagulation and flocculation

The processes before sedimentation are coagulation and flocculation. Coagulation is the process of destabilising the colloids by neutralising the forces that keep the colloids apart. Aluminium oxide and ferric chloride are the most widely used coagulant in the conventional wastewater treatment processes. Flocculation is the formation of bridges between the flocs and binds to form larger agglomerates. Suspended particles are flocculated into larger particles can be removed by filtration or floatation. Polyferric sulphate (PFS) and polyacrylamide (PAM) are the widely used flocculants. However, most of these flocculants and coagulants are not able to remove heavy metals (Chang & Wang, 2007). These processes require the support of other treatment to fully remove heavy metals. In order to overcome the limitation of coagulation, electrocoagulation technique had been introduced. Electrocoagulation involves the formation of coagulants in situ by dissolving electrically iron or aluminium ions from iron or aluminium

electrodes (Chen, 2004). The metals ions are formed at the anodes and hydrogen gas is released from the cathodes. The hydrogen gas that is released assists the floatation of the flocculated particles out of the water. The removal efficiency of heavy metals is able to achieve 99% (Mulligan, 2009). However the electrocoagulation technique requires a huge amount of energy to remove heavy metals (Kim, et al., 2014).

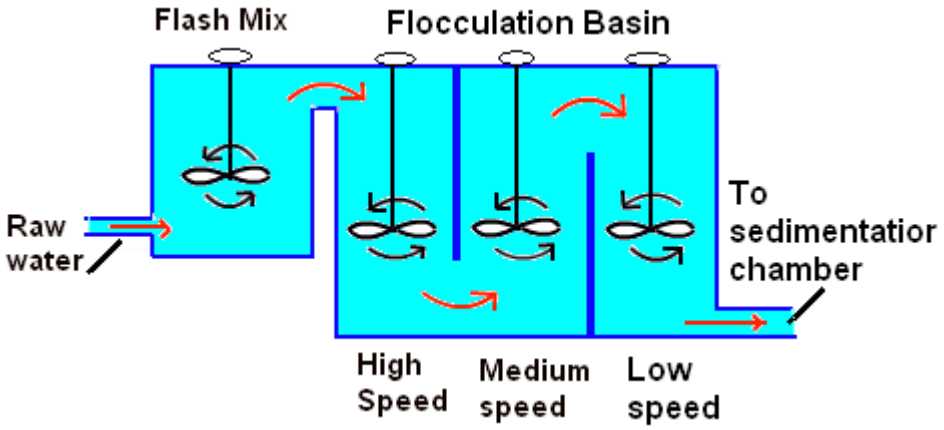

Figure 2.5: Mechanism of Flocculation**(Chemistry.TutorVista.com, 2014)**

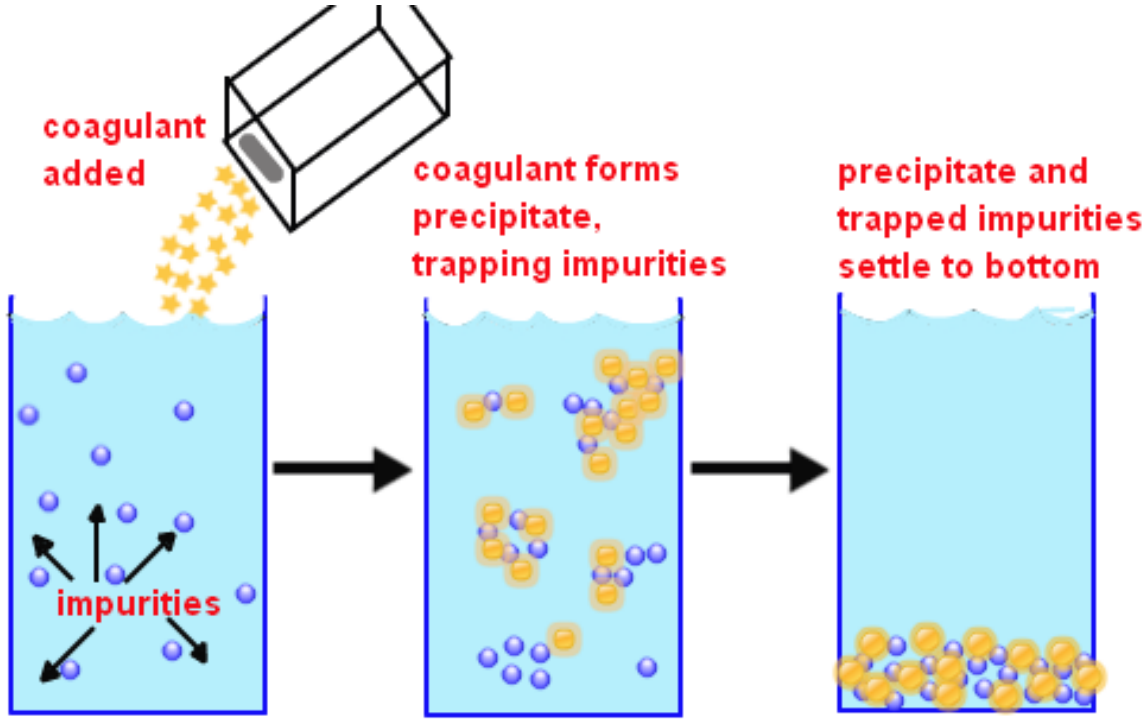

Figure 2.6: Mechanism of Coagulation **(Chemistry.TutorVista.com, 2014)**

Figure 2.7: Coagulation and Flocculation Tank **(Dynamic-des.com, 2014)**

2.2.4 Membrane

Membrane is a thin barrier that allows certain constituents and retains other constituents found in the liquid based on the ionic charge and size of the constituents (Cheryan, 1998). The membrane is separated by one bulk phase with higher concentration of certain constituents and another lower concentration of it as shown in Figure 2.8 (Geankoplis, 2003). In terms of pressure or concentration gradient, the driving force initiates from the chemical potential gradient. Industrial membranes separation processes can be categorized into several groups based on the driving force that initiates the flow of the permeate through the membrane (Matsuura, 1994). In Table 2.2 the types of membrane separation process classified based on the driving force. In general membrane is prone to fouling and concentration polarization (Moreno-Villoslada, et al., 2005).

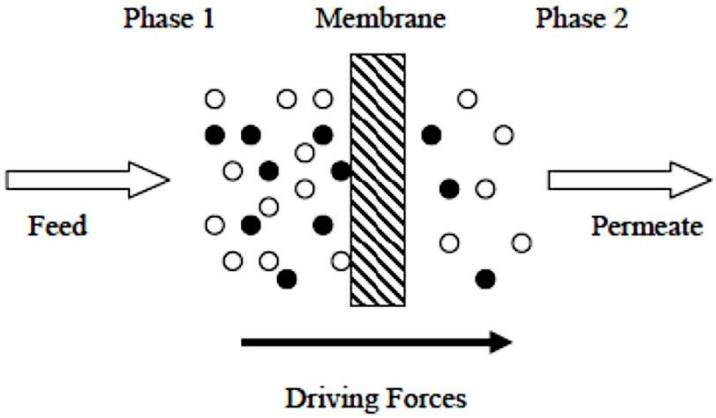

Figure 2.8: Schematic diagram of a two-phase separation system separated by a membrane.**(Tin, 2005)**

Table 2.2: Membrane separation process classified driving force

Type of Driving Force	**Separation Process**
Pressure difference	▪ Reverse Osmosis ▪ Microfiltration ▪ Ultrafiltration ▪ Pervaporation
Concentration difference	▪ Forward Osmosis ▪ Dialysis
Temperature difference	▪ Membrane Distillation
Electric potential difference	▪ Electrodialysis

The membranes that work on the pressure difference can be divided based on the pore size. The classification of the membranes based on the size exclusion of pressure differences are as the following Figure 2.9.

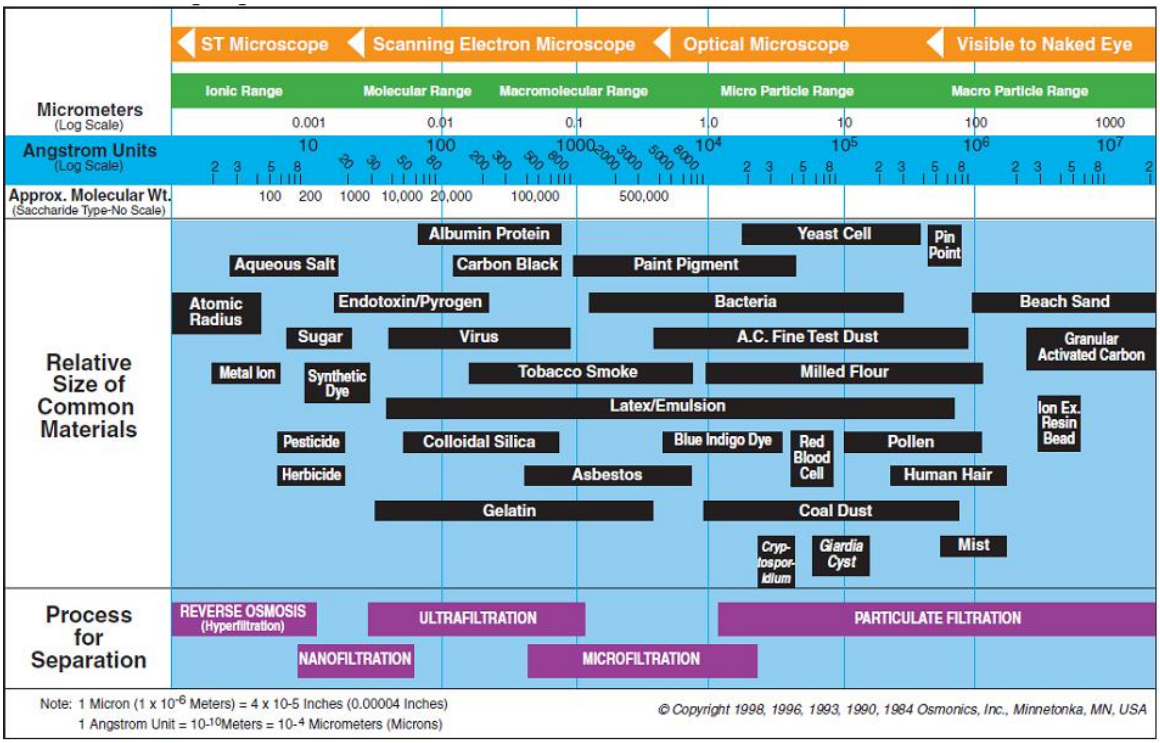

Figure 2.9: Pore Size of Membrane Processes **(Radcliff & Zarnadze, 2004)**

There are a few configurations of membrane which are namely flat sheet, tubular, spiral wound and hollow fiber.

2.2.4.1 Flat Sheet Configuration

Flat sheet membranes are typically synthesized to a filtration system that consists of stacks of modules with a quantity of sheets. Flat sheet has been used in the removal of heavy metals for decades. The cost of running flat sheet membrane will be higher as compared to other conventional techniques as it requires the high pressure application of 20 bars and the module is prone to fouling though it is able to remove heavy metals with the efficiency of more than 96%(Tanninen, et al., 2006). The Figure 2.10 shows the image of flat sheet membrane.